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Copper(I) complexes of *N*-thioacylamido(thio)phosphates and triphenylphosphine

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Abstract

Heteroligand copper(I) complexes of bi- or bis-bidentate acylamidophosphates PhC(S)NHP(S)(OPr-i)$_2$, PhC(S)NHP(O)(OPr-i)$_2$, Et$_2$NC(S)NHP(S)(OPr-i)$_2$, PhNHC(S)NHP(S)(OPr-i)$_2$, *N*-(4-aminobenzo-15-crown-5)-C(S)NHP(S)(OPr-i)$_2$, *N*,*N*-(1,10-diaza-18-crown-6)-[C(S)NHP(S)(OPr-i)$_2$]$_2$, and triphenylphosphine were prepared and characterised. Copper is bound by two PPh$_3$ and one SCNPX (X = O, S) fragment of chelating ligand in all cases. Triphenylphosphine molecules reversibly dissociate in solution. Details of the X-ray structures of (Ph$_3$P)$_2$Cu[PhC(S)NP(S)(OPr-i)$_2$] and (Ph$_3$P)$_2$Cu[Et$_2$NC(S)NP(S)(OPr-i)$_2$] are reported.
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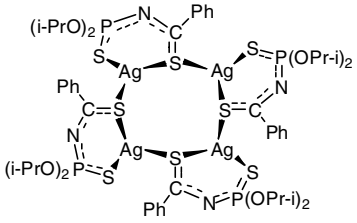
Keywords: Copper complexes; *N*-phosphorylated thioureas; *N*-phosphorylated amides; Triphenylphosphine; Crystal structures

1. Introduction

N-(thio)phosphorylated (thio)amides (**1**) and *N*-(thio)phosphorylated (thio)ureas (**2**) are known to form complexes with a variety of metals both soft and hard. Many complexes of transition [1–5] and alkaline [5–9] metals with *N*-acylamidophosphinates (the general name of compounds containing XCNPY backbone) have been reported (see Scheme 1). Among them, transition metal complexes with C(S)NHP(S) ligands have been investigated most extensively.

Cu(I) and Ag(I) complexes with **1** and **2** are polynuclear in solid state. Thus, Ag(I) cations with thiobenzamide PhC(S)NHP(S)(OPr-i)$_2$ (**3**) form a tetrameric cyclic complex (**4**) [10]. The silver atom in **4** has trigonal configuration. A similar cyclic structure has been found in the trimeric complex of Cu(I) (**5**), obtained with the *N*-thiophosphorylated thiourea **2a** (both R = Et; R′ = OPh) [11]. The copper atoms of **5** adopt a trigonal configuration as well. The alteration in the ring size for **4** and **5** in comparison with each other can be explained both by the difference in ligand structure and in ionic radii of Cu(I) and Ag(I) cations.



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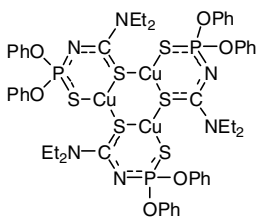

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Complexes of monovalent copper are of interest as catalysts of numerous processes including homolytic C–Hal (Hal = Cl, Br) bond cleavage in polyhaloalkanes [12]. *N*-thiophosphorylated bis-thioureas containing a crown ether

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